REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
	Technical Papers	

4. TITLE AND SUBTITLE

Please see attached

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

5d. PROJECT NUMBER
1011

5e. TASK NUMBER
0046

5f. WORK UNIT NUMBER
346204

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/PRS
5 Pollux Drive
Edwards AFB CA 93524-7048

8. PERFORMING ORGANIZATION REPORT

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
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10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S NUMBER(S)
Please see attached

12. DISTRIBUTION / AVAILABILITY STATEMENT

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13. SUPPLEMENTARY NOTES

14. ABSTRACT

20030116 039

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
					Leilani Richardson
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER *(include area code)*
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MEMORANDUM FOR PRS (In-House Publication)

FROM: PROI (TI) (STINFO) 04 Dec 2000

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-2000-231**
Hawkins, T., "Advanced Propellants"

Visit by Swedish Diplomats to AFRL **(Statement A)**
(AFRL/Edwards, 05 Dec 2000)

1. This request has been reviewed by the Foreign Disclosure Office for: a.) appropriateness of distribution statement, b.) military/national critical technology, c.) export controls or distribution restrictions, d.) appropriateness for release to a foreign nation, and e.) technical sensitivity and/or economic sensitivity.
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APPROVED/APPROVED AS AMENDED/DISAPPROVED

____

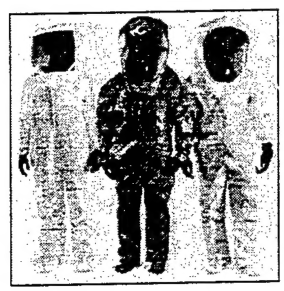
PHILIP A. KESSEL Date
Technical Advisor
Propulsion Science and Advanced Concepts Division

ADVANCED PROPELLANTS

5 December 2000

Dr. Tom Hawkins
Sr Research Chemist
Air Force Research Laboratory

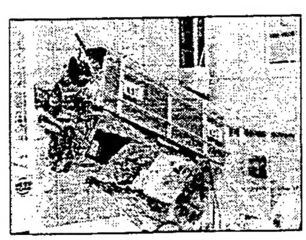
Problem



- Low Performance of SOTA Propellant
  - Low D*Isp
- Increased Operations Costs:
  - Carcinogenic Vapor (Respiratory Route)
  - Dermal Toxicity
  - Strong Reducing Agent
  - Flammable (LEL = 4.7%, UEL = 100%)
- On-Orbit Propulsion Systems Affected

System	Mission
FltSatCom	Military Comm
STARDUST	Deep Space Probe
INTELSAT	Commercial Comm
HEAO-B	X-Ray Astronomy

- Hundreds of Satellites Use Hydrazine for RCS & ACS



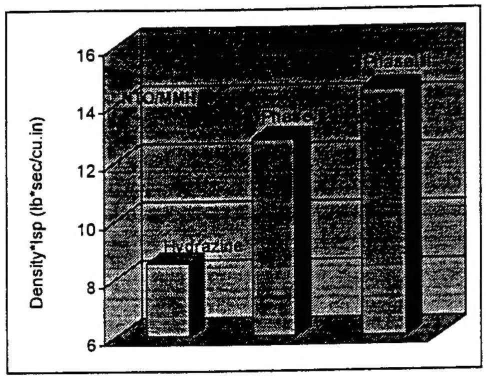
Monopropellant Performance Objectives

- Increase Density Isp of New Monopropellants for IHPRPT Demonstration:

  50% by 2005

  >70% by 2010

- New Monopropellants to Have Reduced Toxicity- Allowing Operations w/o SCAPE-suited Crews



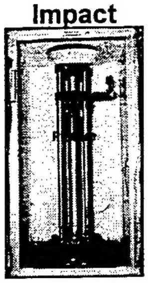
USAF is Lead for IHPRPT Monopropellant Development

Desirable Monopropellant Properties

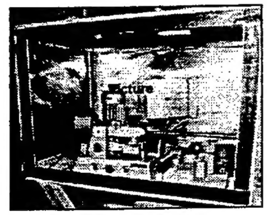
Characteristic	Objective
Density Isp [300 psi-vac; exp=50]	>70 % (Over SOTA)
Vapor Toxicity	Does Not Require SCBA
Carbon Content	No Solid Carbon Forms in Theoretical Exhaust
Melting Point	< 2°C
Detonability [NOL Card Gap]	Class 1.3; (Prefer 24 Cards Maximum (E_{50}))
Impact Sensitivity [Drop Weight]	20 kg-cm Minimum (E_{50})
Adiabatic Compression [U-Tube Test]	No Explosive Decomposition (Pressure Ratio of 35)
Thermal Stability	< 2% by wt. Decomposition for 48 hrs at 75 °C
Critical Diameter	No Propagation in Lines of < 0.75 inch Diameter

Ingredient/Propellant Testing

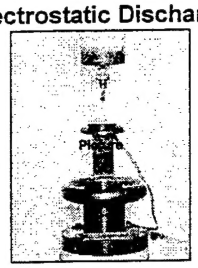
Impact



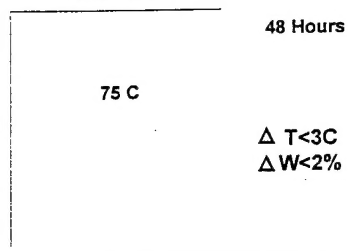
Friction



Electrostatic Discharge



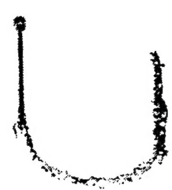
Thermal



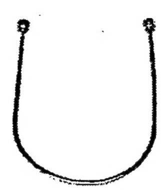
Adiabatic Compressibility

- Designed/Constructed Apparatus in FY00

- Propellant Sensitive to Rapid Compression



- <u>Desired Result</u>: Insensitive to Rapid Compression



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Propellant Testing

Shock to Detonation Tests

- All current solid rocket propellants are divided into two hazard classifications (1.1 or 1.3)
- Two tests are used to distinguish between classes 1.1 and 1.3.

Detonation Test

Blasting Cap
Propellant Cube
Lead Cylinder

Dented 1/8" or more is class 1.1

Card Gap Test

Blasting Cap
Explosive Charge
Cards
Propellant
3/8" Steel Plate
Wood Stand

70 (0.7") Cards or more is class 1.1

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R&D Strategy For Reduced Toxicity Monopropellants

Technical Challenges

- High Toxicity and Vapor Pressure of N_2H_4 Creates High Costs
- Performance Limited by Low Energy Density (8.4 $lb_f s/in^3$)
  - Need 14.4 $lb_f s/in^3$ by 2010
- Highly Ionic Solutions Tend to Have High Melting Points

Approaches

- Use Ionic Compounds with Extremely Low Vapor Pressures and Structures of Reduced Toxicity versus Hydrazine
- Target Energetic Structures Which Confer High Isp
  - High N Content Cations
  - Anions (e.g., $C(NO_2)_3^-$, NO_3^-, $N(NO_2)_2^-$)
- Employ Miscible and Low Melt Point Components

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PHASE II Monopropellant

ACCOMPLISHMENT	SIGNIFICANCE
Synthesis/Delivery of 12 high-N salt compounds for additional toxicological screening at AFRL/HEST	•Additional toxicity data on new propellants/compounds •Supports development of QSAR for new propellant molecules' toxicity
Evaluated monopropellant (Swedish Space Corp)	•Has Phase II performance •High solution miscibility temperature with hazardous solid residue
Produced liquid salt-type propellant for successful thruster test	•Catalytic ignition verified •Spurs hardware development •Patent issues being worked

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Monopropellant Properties

Properties	AFN1	AFN2	Hydrazine
Density , g/cc	1.43	1.46	1.01
Viscosity, cp	8.6	23.1	0.97
Chamber Temp. (Theoretical) , K	2070	2083	883
Carbon Content of Exhaust; (b)	none	none	none
Impact Sensitivity*, kg-cm (5 negatives)	>200	60	>200
Friction Sensitivity, N (5 negatives)	318	300	>371
NOL Card Gap (at 69 Cards)	negative	negative	negative
Thermal Stability, %wt loss/48hr,75°C	< 2.0	< 2.0	(< 0.1)
Melt Point, C	5 (c)	<-22	1

a: Theoretical, calculated with 300psi chamber pressure, exhaust to vacuum, 50/1 expansion
b: as soot or solid carbon (by theoretical computation)
c: by DSC; melt transition was broad, melt peak reported
*: For reference, n-propylnitrate had an impact sensitivity of 8 kg-cm

AFN-Based Propellants Display Acceptable Safety/Sensitivity Properties For Continued Development

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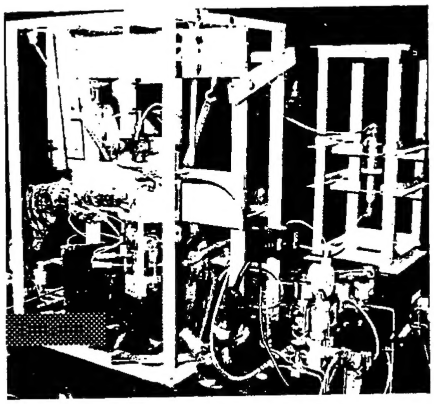
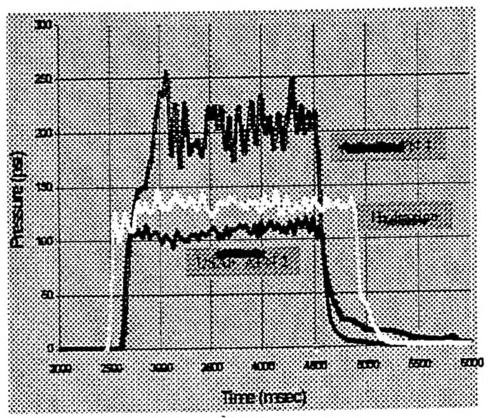
Monopropellant Thruster Testing

Monopropellant Thrust Stand





AFRL Fabricated Thruster and Initiated Testing

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Catalyst Material Development

Contract Program Objectives

- SELECT CANDIDATE HIGH TEMPERATURE MATERIALS SUITABLE FOR CATALYTIC COMBUSTION OF AFRL MONOPROPELLANT
- MANUFACTURE AND SCREEN CATALYST/THERMAL BED SAMPLES
- EVALUATE PERFORMANCE OF DOWNSELECTED CATALYSTS IN THRUSTER FIRINGS WITH AFRL MONOPROPELLANT

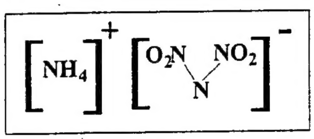
Monolithic Catalyst Bed

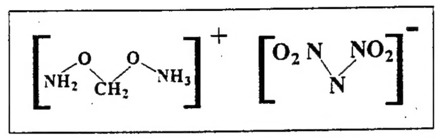
AFRL Collaboration Activity in FY01

- EVALUATES CATALYST MATERIALS
- SUPPLIES PROPELLANT/COMPOUNDS FOR CATALYST EVALUATION

PHASE III MONOPROPELLANT
Ingredient R&D

- Synthesizing/Evaluating dinitramide-based salts
- Many such salts (or salt-based monopropellants) exhibit 'challenging' safety properties
    - Performed evaluations with ADN and MBO salts





Methylene bisoxamine $H_2C(-ONH_2)_2$

Dr. C.S. McDowell et.al. original work published as U.S.patents in 1973, in which the detailed synthesis of MBO selected salts

$CH_3CN + CH_3CH_2\text{-}OH \longrightarrow CH_3C(=NH{\cdot}HCl)OCH_2CH_3$

$CH_3C(=NH{\cdot}HCl)OCH_2CH_3 + H_2N\text{-}OH{\cdot}HCl \longrightarrow CH_3C(=N\text{-}OH)OCH_2CH_3 + NH_4Cl$

$2\ CH_3C(=N\text{-}O^- K^+)OCH_2CH_3 + CH_2Br_2 \longrightarrow [CH_3C(O\text{-}CH_2CH_3)=N\text{-}O]_2\text{-}CH_2 + 2\ KBr$

$[CH_3C(O\text{-}CH_2CH_3)=N\text{-}O]_2\text{-}CH_2 + 2\ HCl(aq) \longrightarrow H_2C(O\text{-}NH_3)_2Cl_2$

$H_2C(O\text{-}NH_3)_2Cl_2 + 2\ KOH \longrightarrow H_2C(O\text{-}NH_2)_2$

MBO bis(dinitramide) $[H_2\text{-}C(O\text{-}NH_3)_2][N(NO_2)_2]_2$

- Russians apparently synthesized through one or two routes:

- Metathesis with silver salts:

$$AgN(NO_2)_2 + H_2C(O\text{-}NH_3)_2Cl_2 \longrightarrow [H_2\text{-}C(O\text{-}NH_3)_2][N(NO_2)_2]_2 + 2\,AgCl$$

- Or, ion exhange:

$$H_2C(O\text{-}NH_2)_2 + 2\,\text{"}H\text{-}N(NO_2)_2\text{"} \longrightarrow [H_2\text{-}C(O\text{-}NH_3)_2][N(NO_2)_2]_2$$

- Reported (1995) as a colorless oil with a melting point of 20° C.

Dinitramide Salts of MBO

USAF production via cation exchange / neutralization

$$H_2C(O\text{-}NH_2)_2 + 2\,\text{"}H\text{-}N(NO_2)_2\text{"} \longrightarrow [H_2\text{-}C(O\text{-}NH_3)_2][N(NO_2)_2]_2$$

Bis-dinitramide Salt:

Appearance: White crystals

M.P. 95° C

Impact: < 5 kg-cm (detonated with a light hammer blow)

DSC Exotherm: 103 °C

Mono-dinitramide Salt:

Appearance: White crystals

M.P. 96° C

Impact: 12 kg-cm (very friction sensitive)

DSC Exotherm: 119 °C

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High Performance Monopropellants -Summary-

- Continue work in monopropellant development & characterization
  - Promising, new approaches
    - Incorporating high energy density molecules
    - Encouraging initial propellant properties
    - Performance potential meets/exceeds bipropellant
      - Simpler, lighter propulsion system
  - Critical work remains
    - Stability, material compatibility, rheology
    - Propellant ignition , high temperature catalyst/materials
      - Teamed with industry

Work with Industry for Successful Technology Demonstration